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Effects of Structural Deformation and Tube Chirality on Electronic Conductance of Carbon Nanotubes

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ABSTRACT

A combination of large scale classical force-field (UFF), density functional theory (DFT) and tight-binding Green's function transport calculations is used to study the electronic properties of carbon nanotubes under the twist, bending and AFM-tip deformation. We found that in agreement with experiment a significant change in electronic conductance can be induced by AFM-tip deformation of metallic zigzag tubes and by twist deformation of armchair tubes. The effect is explained in terms of bandstructure change under deformation.

Keywords: nanotube, molecular dynamics, tight-binding, Green's function, sensor

1 INTRODUCTION

A recent experiment involving a suspended metallic nanotube deformed by an Atomic Force Microscope (AFM) tip [1], revealed that the conductance of the tube may decrease by nearly two orders of magnitude. The effect was found to be completely reversible, i.e., through repeated cycles of AFM-deformation and tip removal, the electrical conductance displayed a cyclical variation with constant amplitude. Based on the tight-binding simulations, this effect was explained by the formation of local sp^3 bonds due to the mechanical pushing action of the tip. The sp^3 coordination ties up delocalized p-electrons into localized s-states. This would naturally explain the large drop in electrical conductivity, as verified by explicit transport calculations.

Recently, we performed atomistic simulations using a combination of classical force-field, Density-Functional-Theory (DFT) and Green's function technique to study the effect of structural deformation and chirality on electronic conductance of carbon nanotubes [2]. We showed that carbon atoms remain essentially sp^2 coordinated in either bent tubes or tubes pushed by an atomically sharp AFM tip. Subsequent transport calculations revealed that for armchair tubes there is no significant drop in conductance, while for zigzag tubes the conductance can drop by several orders of magnitude in AFM-pushed tubes.

In this paper, we give new details of our previous work and also extend our simulations to study the conditions under which an armchair nanotube becomes semiconducting. The results of large scale atomistic simulation are then followed by a simple π-orbital analysis of nanotube bandstructure under deformation.

2 RESULTS

The simulations were carried out on (6,6) armchair and (12,0) zigzag tubes of 2400 atoms. Initially the straight tube was relaxed with the UFF.

To simulate bending, two halves of the tube were then rotated by equal and opposite angles about an axis perpendicular to the tube and passing through the center of mass of the initial straight tube. For twist, two halves of the tube were twisted by equal and opposite angles around the axis of the tube. At each end of the tube, a contact region defined by a unit cell plus one atomic ring was fixed and the whole tube relaxed with the UFF. For AFM-tip deformation, the 15-atom Li-needle was initially aimed at the center of a hexagon on the bottom-side of the middle part of tube as in [3]. The Li-needle was then displaced by an amount δ toward the tube along the needle-axis, resulting in a deformation angle $\theta = tan^{-1}(2\delta/L)$, L being the unstretched length of the tube. The whole tube was then relaxed by UFF keeping the needle atoms and the end contact regions of the tube fixed. After that, a cluster of 132 atoms for the (6, 6) and a cluster of 144 atoms for the (12, 0) were cut out from the middle of the tubes and further relaxed with Accelrys' DFT code DMol^3 [4]. Fixing the relative positions of contact region atoms at the same value as in an undeformed tube guarantees that contacts may be approximated by ideal semi-infinite carbon nanotube leads and that all possible contact modes are coupled to the deformed part of the tube.

After doing classical force-field simulations, we performed calculation of transmission and DOS using Green' function technique [5] within the nearest-neighbor sp^3-tight-binding Hamiltonian in a non-orthogonal basis. The parameterization scheme explicitly accounts for effects of strain in the system through a bond-length-dependence of the Hamiltonian and the overlap matrices H_{ij} and S_{ij}, as in [6]. Other tight binding parameterization schemes [7] give qualitatively the same results. We start with finding the Green's function of and transmission through the nanotube, assuming that it is coupled to semi-infinite undeformed nanotube

contacts. The coherent conductance then was found using Landauer- Büttiker formula:

$$G = \frac{2e^2}{h}\int_{-\infty}^{\infty} T(E)\left(-\frac{\partial f_0}{\partial E}\right)dE \qquad (1)$$

2.1 AFM-tip deformation and bending

The analysis of C atom coordinates in deformed tubes after the relaxation reveals that the bond length between each atom and its three nearest neighbors may vary between 1.4-1.7 Å, while the distance to the fourth neighbor never becomes shorter than 2.2 Å. We infer from this that sp^3 coordination is absent in any of the simulated cases.

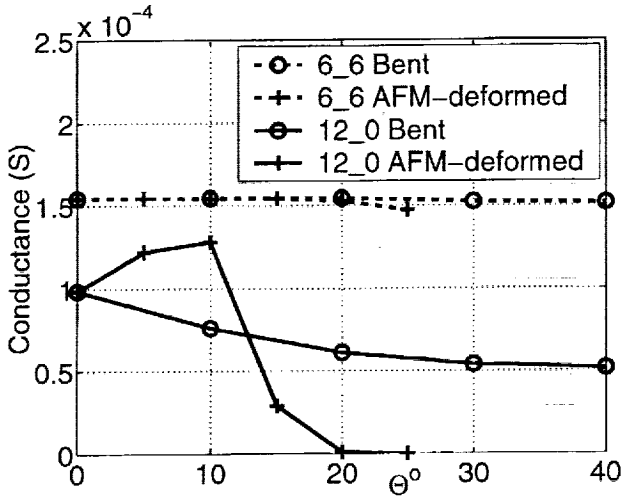

Figure 1: Conductance of armchair (dashed) and zigzag (solid) nanotubes under bending (circle) and AFM-tip (cross) deformation as a function of the deformation angle. The drop of conductance for zigzag nanotube is more than four orders of magnitude at $\theta = 25^o$.

The resulting conductance, shown in Fig. 1, for the armchair tube, is lowered only by 1% for the tube bent by 40^o and 5% for a tube tip-deformed by 25^o. Under the same deformations, drop in conductance, for the zigzag tube, is much higher, being 52% under bending, and more than four orders of magnitude under tip-deformation.

To gain insight into the behavior, we computed transmission through 5 unit cells (240 atoms) in three different regions of the AFM-tip deformed (12, 0) tube for $\theta = 25^o$: (1) undeformed contact, (2) highly deformed tip region, and (3) the uniformly stretched straight regions on either side of the tip-deformed region. In these calculations, the deformed region was cut out and coupled to undeformed semi-infinite leads. In Fig. 2, transmission through both tip region and the straight part show a bandgap opening, which proves that the conductance drop occurs everywhere in the tube, rather than in the tip-deformed region alone. The same bandgap is also observed in the local DOS in the three different regions when the whole tube is coupled to the contacts. We thus conclude that the conductance drop in AFM-tip deformed metallic zigzag nanotubes occurs due to simple stretching of the total length of the tube.

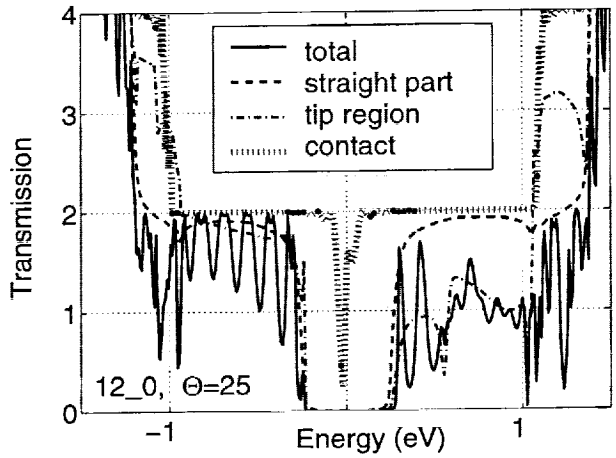

Figure 2: Transmission through three different regions of (12,0) AFM-tip deformed tube at $\theta = 25^o$. 5 unit cells (240 atoms) were cut out and coupled to undeformed leads.

2.2 Twist deformation

As a result of twist deformation, all three bonds of a carbon atoms become nonequivalent. The distribution of the bond lengths for all atoms in the tube is shown in Fig.3. In these calculations, the twist angle is defined as the angle between the orientations of the left and right undeformed contacts.

Fig.4 displays the computed conductance (at T=300K) of a twisted (6,6) nanotube as a function of a twist angle. The conductance drops by 35 times at the angle of 120^o.

The inset in Fig.4 shows that the conductance drop is due to the bandgap opening in the vicinity of Fermi surface in transmission and the DOS. The gap increases with the twist angle and is about 250meV at the angle of 120^o.

π-orbital analysis

In order to explain the conductance behavior under deformation, we have analyzed the bandstructure of armchair and zigzag nanotubes within a π-orbital model. Starting from the band structure of the 2D graphene under deformation [8], one can derive the following dispersion relations for the crossing subbands [9] (*a'* below is the strained periodic repeat length along the nanotube axis):

$$E(k)=\pm t_2\{\,1+\alpha^2+\beta^2-\alpha\beta-2\alpha\cos(\pi/3-\sqrt{3}ka'/2-2\beta\cos(\pi/3+\sqrt{3}ka'/2)\}^{1/2} \quad (1)$$

for metallic zigzag nanotube and

$$E(k)=\pm t_2\{\,1+(\alpha-\beta)^2-2(\alpha+\beta)\cos(ka'/2)+4\alpha\beta\cos^2(ka'/2)\}^{1/2} \quad (2)$$

for armchair nanotube.

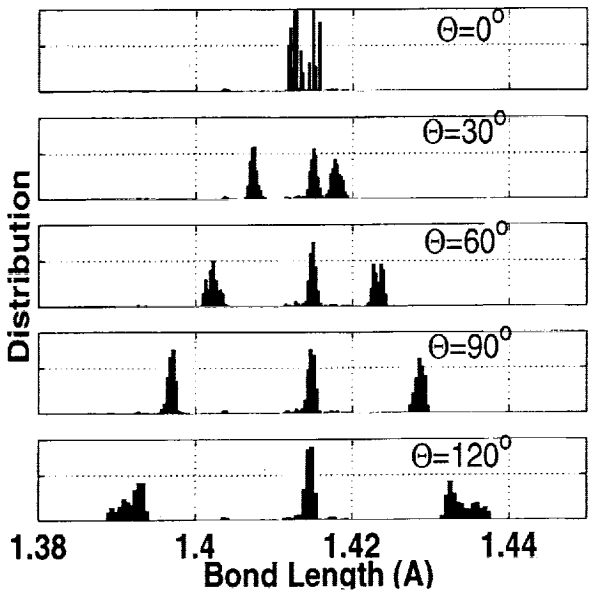

Figure 3: The bond length distribution in armchair nanotube under the twist deformation. All three bond of a carbon atom become nonequivalent.

Here $\alpha=t_1/t_2$ and $\beta=t_3/t_2$ are the ratio of nonequivalent hopping parameters. For the sake of simplicity, the hopping parameters may be assumed to be inversely proportional to the bond length squared [10]. In the case of uniform stretching, $\alpha=\beta>1$ for a zigzag tube and $\alpha=\beta<1$ for an armchair tube. Eq. 1 will result in a nonzero energy at any value of ka', hence a bandgap. In contrast, in Eq. 2 there is always a value of ka' which will make energy zero and the nanotube will remain metallic as long as $\alpha>1/2$. This explains the difference in conductance behavior between AFM-tip deformed zigzag and armchair tubes. Under bending conditions, the stretching is very weak and happens only in a tiny region. Therefore bending leads only to minor decrease in conductance for all chiralities. In the case of twist deformation, $\alpha>1$ and $\beta<1$. Using Eq.2 and the bond length distribution in Fig.3, we compute the dispersion relation of the armchair nanotube, which is shown in Fig.5. The value of t_0 was 3eV. The bandgap opening agrees qualitatively and quantitatively with the Green's function calculations. Eq. 1 for metallic zigzag nanotube will also result in a bandgap opening, although the effect will be much smaller because of the second order dependence of the bandgap on the deformation [9]. In general, as chiral angle changes continuously from zigzag to armchair case, so does the conductance of the tube.

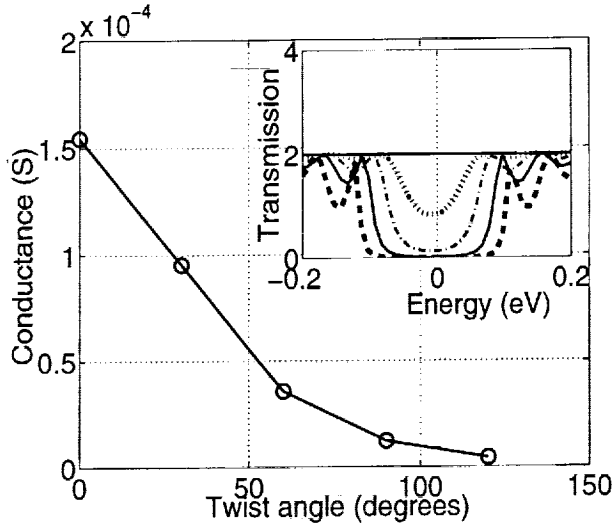

Figure 4: Electronic conductance in an armchair nanotube under the twist deformation. The inset shows the energy dependence of transmission through an armchair nanotube at different twist angles.

3 CONCLUSION

In conclusion, we performed large scale atomistic modeling of carbon nanotubes under various types of deformation. The results obtained agree well with simple π-orbital model. We found that under the AFM-tip deformation, conductance of metallic zigzag nanotubes drops by 4 orders of magnitude due to stretching, similar to the experiment in [1]. Under the twist deformation, an armchair nanotube shows a conductance drop by a factor of 35. These effects have important implications for the application of nanotubes as electromechanical sensors and also allow one to determine the chirality of a tube experimentally.

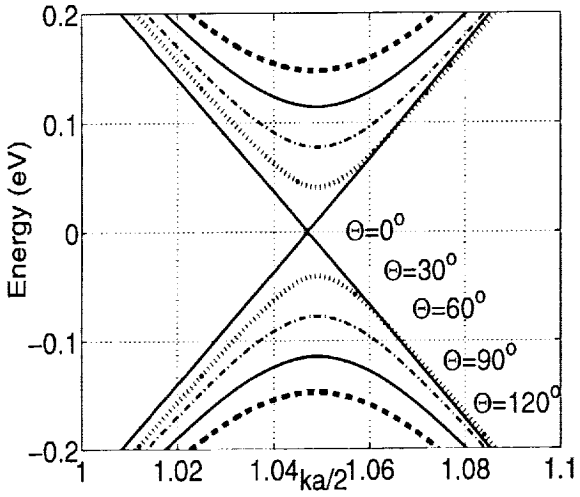

Figure 5: Energy dispersion for crossing subbands of an armchair nanotube under the twist deformation at different twist angles.

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